The Isolation of Phyllocladene from the Leaf-oil of *Podocarpus hallii* and its Significance on the Botanical Classification of this Species.

By LINDSAY H. BRIGGS.

[*Read before the Auckland Institute, August 21, 1940; received by the Editor, August 13, 1940; issued separately, December, 1940.*]

AT the present time there appears to be some difference of opinion concerning the botanical classification of *Podocarpus hallii*. The first suggestion that it is a species similar to but distinct from *P. totara* came from J. W. Hall, of Shortland, after whom the species has been named by Kirk (1889), who concurred with this view and published the first description of this species and the major points of difference between it and *P. totara*. At the same time, Kirk suggested that the species *P. cunninghamii*, growing in the Ruahine Ranges and first named by Colenso in 1884, was identical with *P. hallii*. Apparently only the Maoris of Stewart Island have regarded *P. hallii* distinct from *P. totara*, calling the former "totara-kiri-kotukutuku" (*Fuchsia*-barked totara) and the latter with thicker bark "amoka," although Colenso also records the former name for *P. cunninghamii*.

Since that time, even leading botanists have differed in their views as to the existence of *P. hallii* as a distinct species. Cheeseman (1925) regards it merely as a variety of *P. totara*, with which Pilger agrees (1903). In the same way, Cheeseman considers the actual type specimens of *P. cunninghamii* of Colenso's herbarium as those of *P. totara*.

The application of a knowledge of the chemical constituents of plants in their botanical classification has been well exemplified in the case of the eucalypts by Baker and Smith (1920). In their experience, species which could not be distinguished botanically yielded essential oils containing distinctly different chemical constituents, and for this reason were given the status of a true species. This work has been extended by Penfold (published mainly in the *Transactions of the Royal Society, New South Wales*), who has modified somewhat the conclusions of Baker and Smith. For example, he has made the interesting discovery (1936) that the oils obtained from the leaves of different branches of the same tree sometimes show considerable variation in their chemical constituents so that care must be exercised in the use of these constituents as an aid to botanical classification. In most cases, however, the differences were found to be in the large percentage variation of the constituents, and only rarely to the appearance of a constituent not found in the type specimen.

The essential oil of *P. totara* was first investigated by Aitken (1929), who obtained among other constituents the liquid diterpene, totarene, b.p. 180°/12 mm., but Beath, in a later investigation (1933), isolated the solid diterpene, rimuene, m.p. 55·5°, which had previously been obtained from the leaf-oil of *Dacrydium cupressinum* (McDowall and Finlay, 1925; Carrie, 1932).

The leaves of *P. hallii* have now been found to contain an essential oil from which another solid diterpene, phyllocladene,

m.p. 96·5°, has been isolated, the same hydrocarbon being obtained from the leaves of different trees. This diterpene also occurs in the leaf oil of *Phyllocladus rhomboidalis* (Baker and Smith, 1910), *Phyllocladus alpinus* (Briggs, 1937; Brandt, 1938), *Dacrydium biforme* (Goudie, 1923; Aitken, 1928), *Dacrydium colensoi* (Blackie, 1929), *Sciadopitys verticillata* (Nishida and Uoda, 1935, 1936) and *Araucaria excelsa* (Briggs, 1937).

Rimuene and phyllocladene are closely related, both being isomerised by acids to isophyllocladene, m.p. 110–111°.

The isolation of phyllocladene from *P. hallii* is therefore the first record of this diterpene in a species of *Podocarpus,* and since it differs from rimuene obtained from *P. totara,* it would appear from chemical evidence at least that *P. hallii* should be given the status of a separate species.

Experimental.

Leaves from *P. hallii* growing in the Waitakere Ranges near Auckland were steam distilled in the usual way, the leaves from different trees being treated separately. If the steam distillate were collected in fractions, the oil from the last fraction completely solidified. This material after a single crystallisation from methyl alcohol had m.p. 96·5° C., undepressed by an authentic specimen of phyllocladene. The same hydrocarbon was obtained from each of the separate distillations. The rotation, $[\alpha]_D^{25^\circ}$ +15·6° (l = 1 dcm., c = 1·795 in chloroform), agrees also with the values recorded for phyllocladene. The identity was confirmed by conversion into isophyllocladene by boiling for a few minutes with 10% alcoholic sulphuric acid. The material which separated on cooling, crystallised from ethyl alcohol in long needles, m.p. 110–111° C., undepressed on admixture with an authentic specimen.

The author is indebted to Mr. G. Dingley, M.Sc., for collection of part of the material and to the Chemical Society for a grant.

References.

Aitken, H. A. A., 1929. *J. Soc. Chem. Ind.,* 48, 344T.
Aitken, P. W., 1928. *J. Soc. Chem. Ind.,* 47, 223T.
Baker, R. T., and Smith, H. G., 1920. *A Research on the Eucalypts and their Essential Oils,* Second Edition.
——— 1910. *A Research on the Pines of Australia,* p. 416.
Beath, G. B., 1933. *J. Soc. Chem. Ind.,* 52, 338T.
Blackie, W. J., 1929. *J. Soc. Chem. Ind.,* 48, 357T.
——— 1930. *J. Soc. Chem. Ind.,* 49, 26T.
Brandt, C. W., 1938. *N.Z. Jour. Sci. Tech.,* 20, 8B.
Briggs, L. H., 1937. *J. Chem. Soc.,* 79.
——— 1937. *J. Soc. Chem. Ind.,* 56, 137T.
Carrie, M. S., 1932. *J. Soc. Chem. Ind.,* 51, 367T.
Cheeseman, T. F., 1925. *Manual of the New Zealand Flora,* Second Edition, p. 111.
cf. ——— 1914. *Illustrations of the New Zealand Flora,* vol. 2, plate 185.
Goudie, B. H., 1923. *J. Soc. Chem. Ind.,* 42, 357T.
Kirk, T., 1889. *The Forest Flora of New Zealand,* p. 13, appendix p. 301.
McDowall, F. H., and Finlay, H. J., 1925. *J. Soc. Chem. Ind.,* 44, 42T.
Nishida, K., and Uoda, H., 1935. *J. Agric. Chem. Soc. Japan,* 11, 489.
——— 1936. *J. Agric. Chem. Soc. Japan,* 12, 308.
Penfold, A. R., and Morrison, F. R., 1936. *Nature,* 138, 1099.
Pilger, R., 1903. *Pflanzenreich,* IV, 5, 84.